Reaction of Ketene with Ethylacetoacetate

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27	$C_6H_6 \rightarrow (C_2H_5)_2O$		10	Acetone	−	−	+	+	++	+		667	20.2
28		E	30		−	−	+	+	++	+		860	19.3
29			60		−	−	+	+	++	+		663	15.0

1 Dried after treating with some solvents.
2 H : Hanging in ketene stream.
E : Immersing in ether.
(3) Speed of ketene gas maintained at about 0.12 mole/10 min.
(4) Washing out ketene polymers with solvents.
(5) Sunlight in midsummer.
(6) (−) : colorless.
(+) : faintly yellow.
(++) : deep yellow.

13. Reaction of Ketene with Ethylacetoacetate

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It is well known that ketene reacts with ethylacetoacetate giving O-acetyl derivative. But there is no information about the formation of C-acetyl derivative in this reaction. As shown in the following descriptions, it was now found that C-acetylation or O-acetylation can be effected according to the conditions, under which ketene and ethylacetoacetate react.

(i) Without catalyst, ketene and ethylacetoacetate did not react near 0°C, but at about 50°C, gave C-acetyl derivative, $CH_3—\overset{\overset{O}{\|}}{C}—\overset{\overset{COCH_3}{|}}{CH}—COOC_2H_5$, and at about 80°C, in a good yield. In this reaction, no O-acetyl derivative was produced.

(ii) In the presence of conc. H_2SO_4, no reaction occurred at 0°C between the reactants, but at 80—90°C, O-acetyl derivative, $CH_3—\overset{\overset{OOCCH_3}{|}}{C}=CH—COOC_2H_5$, was solely obtained in a good yield.

(iii) The sodium salt of ethylacetoacetate suspended in ether reacted with ketene at 0°C, giving C-acetyl derivative solely as the product. The conditions and the results of these reactions mentioned above are summerized in the following Table.

Reactions of ketene with ethylacetoacetate.

Exp. No.	Ethyl-acetoacetate g.(mole)	Catalyst g.(mole)	Ketene g.(mole)	Solvent cc	React. Temp. °C	After-treatment	Products: Fractions (B.P.) 90–100°/20mm g.	n_D	100–110°/20mm g.	n_D	Yield %	M.P. of Cu-Salt	
1	65(0.5)	None	42(1.0)	None	2—4	None	—	—	—	—	—	—	—
2	65(0.5)	〃	42(1.0)	〃	45—49	〃	7	1.4475^{17}	6(2)	1.4680^{17}	15	150—151	C-Acetyl derivative
3	65(0.5)	〃	42(1.0)	〃	80—87	〃	9	1.4590^{14}	23(2)	1.4708^{14}	37.5	150—151	〃
4	65(0.5)	conc. H_2SO_4 1	42(1.0)	None	0	Na_2CO_3	—	—	—	—	—	—	—
5	65(0.5)	1	42(1.0)	〃	75—80	〃	9(1)	$1.4371^{11.5}$	34(1′)	$1.4454^{11.5}$	50	—	O-Acetyl derivative
6	65(0.5)	1	42(1.0)	〃	84—94	〃	13	$1.4352^{15.5}$	44.5	$1.4430^{15.5}$	67(6)	—	〃
7	65(0.5)+Na, 1(0.04)		42(1.0)	Ether 100	0	20%H_2SO_2	5.5	1.4454^{14}	15(3)	1.4617^{14}	24	151—152	C-Acetyl derivative
8	65(0.5)+Na10.5 (0.45)		59(1.4)	300	0	〃	15	1.4521^{12}	24(4)	1.4660^{12}	45.5	150—151	〃
9	Pure Na-Salt 17(0.112)		29(0.7)	100	0	〃	0.5	—	10.5(5)	1.4660^{20}	55	151—152	〃

Data from Literature :

(Name)	(b.p.)	(n_D^{20})	(m.p. of Cu-Salt)
Ethylacetoacetate	80°/20 mm.	1.41937-76	[192]
C-Acetyl derivative	89°/10 mm.	1.4690	[151]
O-Acetyl derivative	94°/10 mm.	1.4420-80	—

(1) 95-105°/25 mm.
(1′) 105-117°/25 mm.
(2) 100-108°/20 mm.
(3) 100-106°/20 mm.
(4) 100-104°/20 mm.
(2) 100—103°/20 mm
(6) 3.5g. of 100-119°/4mm. ($n_D^{15.5}$ 1.4510) was also obtained.